

124
concl.
consisting of a substituted or unsubstituted halogenated allyl and
a substituted or unsubstituted allyl alcohol derivative.--

REMARKS

Claims 1-30 are pending and stand ready for further action on the merits. Support for the proviso which is now recited in claims 1, 3, 5, 7, 8, 11 and 12 can be found in the Examples.

Regarding new claims 25-30, support for these claims can be found in claims 1, 3, 5, 8, 11 and 12, respectively; support for the recitation of the olefins can be found at lines 17-18 of page 17 of the present specification; and support for the recitation that the R¹ group does not act as a nucleophile in the reaction can be found at lines 4-6 of page 4 of the present specification. Support for the recitation of the titanium compound in claims 12 and 30 can be found in claim 5. No new matter has been added by way of the above amendment.

Issues Under 35 U.S.C. § 102

Claims 1, 2, 5-7, 11-16 and 18-20 stand rejected under 35 U.S.C. § 102(b) as being anticipated by Mukaiyama or Corey et al. Applicant respectfully traverses the rejections.

In describing the requirements for rejection of a claim by anticipation, the Manual of Patent Examining Procedure (Section 2131) states:

A claim is anticipated only if each and every element as set forth in the claim is found, either expressly or inherently described, in a single prior art reference (ref. omitted). The identical invention must be shown in as complete detail as is contained in the ... claim (ref. omitted). The elements must be arranged as required by the claim ... (ref. omitted).

Furthermore, in *Ex Parte Levy*, 17 USPQ2d (1461, 1462), the Board of Patent Appeals and Interferences has written:

Moreover, it is incumbent upon the Examiner to identify wherein each and every facet of the claimed invention is disclosed in the applied reference (ref. omitted).

Accordingly, Applicant respectfully indicates, every element in a claim must be found in the reference in order that the reference anticipate the claim. None of the reactions in either Mukaiyama or Corey et al. include the combination of a compound having a carbon-carbon unsaturated bond and a compound having an electrophilic functional group or an electrophilic reagent. Therefore, the references do NOT anticipate the claims, and as such, Applicant respectfully requests that the rejections be withdrawn.

Should the Examiner not find Applicant's arguments persuasive, the Examiner is requested to specifically identify the reactions/reagents which are disclosed in the cited references that render the cited references anticipatory.

Issues Under 35 U.S.C. § 112

Claims 1-4 stand rejected under 35 U.S.C. § 112, second paragraph. Applicant respectfully traverses the rejection.

The Examiner alleges "The composition claimed does not appear to be a catalyst because a catalyst should be the same composition beginning and ending the reaction. This does not appear to be the case with the instant composition." In response, Applicant has enclosed, as Exhibit A, a copy of Hampel et al. (Hampel, C.A. et al., The Encyclopedia of Chemistry, 3rd Ed., 1973, Litton Educational Publishing, Inc., pp. 209-212). Hampel et al. teaches

For many years it has been recognized that certain substances by their very presence are able to alter the rate of chemical reactions ... Berzelius called these substances "catalysts" and named the phenomenon "catalysis" ... It is frequently stated that a catalyst is a substance capable of altering the speed of a reaction without itself necessarily undergoing any chemical change. It must be recognized, however, that according to present points of view, a typical catalyst as it operates in a reaction may well have been altered considerably from the form in which it was added to the reactants.

It is frequently stated that a catalyst is a substance capable of altering the speed of a reaction without itself necessarily undergoing any chemical change. It must be recognized, however, that according to present points of view a typical catalyst as it operates in a reaction may well have been altered considerably from the form in which it was added to the reactants. The changes are especially notable in the composition of the surface layer of a catalyst, though in many instances changes throughout the body of the catalyst may also take place. For example, if an iron catalyst is placed in contact with a mixture of hydrogen and nitrogen at 450°C, the iron immediately becomes covered with a chemisorbed layer of nitrogen, hydrogen and perhaps even ammonia molecules. Furthermore, the catalyst becomes saturated with dissolved nitrogen and dissolved hydrogen. It may even be true that these added gases influence the electronic characteristics of the solid catalysts in such a way as to be controlling factors in the activity of the iron as a catalyst.

A more extreme instance of a change in the catalyst during use is afforded by the iron catalysts that are active in the synthesis of hydrocarbons from mixtures of carbon monoxide and hydrogen. Such a catalyst, which initially consists mostly of iron, changes very rapidly to a mixture of carbides and Fe_3O_4 . A certain small amount of the original alpha-iron also usually persists. It is important to know, however, that during the various changes in the solid phase of the catalysts, the activity often continues at a fairly steady level. It might perhaps be more accurate to say that the solid which is initially added to a reaction and which is commonly called a catalyst undergoes rapid changes in the presence of reacting gases to some form in which the surface becomes a combination of catalyst and reactant atoms in a ratio that is often not known.

The persistence of activity for long periods of time indicates, however, that this surface layer presumably reaches a steady state and does not change extensively, even though the underlying bulk phase, may become altered as a function of time.

Another important characteristic of a catalyst is the fact that a formula weight of catalyst will usually be effective in participating in the transformation of many formula weights of reactants. For example, iron synthetic ammonia catalysts are known to have operated effectively for periods of several years, in the course of which a million or more formula weights of ammonia per formula weight of catalyst were produced. Eventually, catalysts lose their activity due to gradual sintering, accumulation of poisons, the occurrence of side reactions between the catalyst and one or more of the reactants, or the accumulation of products. In practice they may have to be regenerated every few minutes or not for years, depending upon the reactants, the catalyst, and the operating conditions.

Catalysts merely speed reactants toward their normal chemical equilibrium but do not actually alter the position of equilibrium. Thus, for example, if a mixture of three parts hydrogen and one part nitrogen is placed in contact with an iron catalyst at 450°C and a total pressure of one atmosphere, the final equilibrium amount of ammonia will correspond to 0.23% of a gaseous phase. This figure therefore represents the upper limit of the

per cent ammonia that can be produced in a stream of 3:1 hydrogen to nitrogen gas over an iron catalyst at this particular temperature and at atmospheric pressure. It must be kept in mind that in complex reactions a catalyst frequently can yield many products. It does not always follow that the products formed will be those which would be obtained if equilibrium existed among all the various products. For example, cetane can be cracked over a silica-alumina catalyst to a variety of hydrocarbons. It is well known that the ratio of isobutane to normal butane obtained as a reaction product at a given temperature is always considerably in excess of the ratio that would exist if these gases were in contact with the catalyst long enough to permit sufficient isomerization of iso- to normal butane. It so happens in this instance that under operating conditions the cracking reaction occurs at a relatively faster rate than the isomerization reaction among the reaction products.

Catalysts may be solids, liquids or gases. If the reactants and catalysts comprise two separate phases, as in the case of gases reacting over solids, or liquids reacting in the presence of finely divided solids, the phenomenon is frequently referred to as *heterogeneous* catalysis. On the other hand if the catalyst and the reactants are all dispersed as a homogeneous phase, the process is usually designated as *homogeneous* catalysis. Iron catalysts for the synthesis of ammonia represent a good example of heterogeneous catalysts; on the other hand, acids in solution may act as catalysts for different components of a liquid phase by a process of homogeneous catalysis. Most of the present discussion is devoted to heterogeneous catalysis but a few brief remarks will also be made relative to some of the essentials of homogeneous catalysis.

Preparation and Nature of Solid Catalysts. Catalysts may consist of elements, compounds or amorphous mixtures of complexes or compounds. Among the elements, the metals are particularly useful as catalysts. Among compounds, metallic oxides and metallic sulfides are outstanding. Probably the principal example of an amorphous mixture of complexes or compounds is the silica-alumina catalyst used in cracking hydrocarbons.

One important characteristic of catalysts is that they are usually highly specific in their activities. For example, a catalyst may well be active for the hydrogenation of certain bonds of organic compounds and yet completely inactive for the hydrogenation of other bonds. Thus, for example, copper chromite will readily hydrogenate carbonyl groups on organic molecules but is relatively inactive for the hydrogenation of carbon-carbon double bonds and completely inactive for the hydrogenation of benzene. Metallic nickel on the other hand will hydrogenate all three types of bonds. Again, an alloy containing 80% copper and 20% nickel will rapidly hydrogenate ethylene but not styrene. This property of a catalyst—to be specific in regard to its action—is extremely important. In those systems in which a multiplicity of activities might be involved, this specificity of catalysts is for the most part an inherent characteristic of a given surface. Moreover, it is also dependent to a certain extent upon the pore size and pore distribution of the catalyst. For example, catalysts for partial oxidation

211
shc
to
into
wh
cat
T
way
the
bot
of t
of
whi
in a
are
alur
E
of a
tion
tive
mat
addi
amp
and
ide
porc
pron
activ
redu
taini
mote
some
pron
At
the r
actio
moni
iron
Re
there
solid
actua
the r
the n
mote
amor
tation
of sui
Ca
invol
a way
tion c
traces
will u
a met
may l
by so
short
actant
by su
For e
hydro
poison
of the
a stre
nitrog
and th
during
alumin

ed in a stream
an iron cata-
nd at atmos-
mind that in
tly can yield
allow that the
would be ob-
ll the various
cracked over
of hydrocar-
of isobutane
on product at
ably in excess
gases were in
gh to permit
ormal butane.
der operating
rs at a rela-
tion reaction

gases. If the
two separate
g over solids,
finely divided
referred to as
r hand if the
dispersed as a
usually desig-
catalysts for
good example
r hand, acids
ifferent com-
s of homoge-
discussion is
t a few brief
some of the

alysts. Cata-
nds or amor-
compounds.
particularly
nds, metallic
ding. Prob-
orphous mix-
he silica-alu-
rbons.
alysts is that
eir activities.
active for the
organic com-
or the hydro-
mple, copper
bonyl groups
inactive for
ouble bonds
ogenation of
er hand will
Again, an
nickel will
yrene. This
in regard to
In those sys-
ies might be
for the most
ven surface.
ertain extent
a of the cata-
lial oxidation

should presumably have a pore size sufficiently large to lower the probability of oxidation of the desired intermediate product to carbon dioxide and water while it is passing out of the pore structure of the catalyst into the main gas stream.

Traditionally, catalysts are prepared in such a way as to produce large surface areas. They are therefore usually either finely divided or porous or both. For the maintenance of a large surface area of the catalytic component, use is frequently made of substances which in themselves are inert, but which are capable of supporting the active catalyst in a form that resists sintering. Common supports are alumina, kieselguhr, silica gel, and even silica-alumina catalysts.

Evidence very strongly suggests that the activity of a catalyst is often centered in only a small fraction of the catalyst surface. The nature of these active points or active regions is still very much a matter of dispute. Sometimes they are created by adding impurities known as *promoters*. For example, the addition of about 1% of potassium oxide and 1% of some inert oxide such as aluminum oxide to an iron oxide catalyst yields on reduction a porous iron solid partially covered with these added promoter materials. Such catalysts are much more active at high pressure than those produced by the reduction of pure iron oxide or those catalysts containing, for example, only aluminum oxide as promoter. It thus appears that one must attribute some intrinsic activity to the interface between the promoter components and the metal surface.

Another proposal is that only certain planes on the metallic catalysts are active for a particular reaction. For example it has been suggested that ammonia synthesis takes place on the 111 planes of iron rather than the 100 or 110 planes.

Regardless of the nature of the active regions, there is no question but that the surface of most solid catalysts is very nonuniform in activity. The actual preparation of catalysts frequently involves the reduction of metallic oxides or compounds to the metal form after the addition of necessary promoters. The oxides themselves are prepared in an amorphous or finely crystalline condition by precipitation under proper conditions and in the presence of suitable promoters.

Catalysts are usually subject to poisoning. This involves the deposition of certain impurities in such a way as to render the active centers or active portion of the catalyst surface inactive. For example, traces of hydrogen sulfide in a stream of hydrogen will usually cause a rapid decrease in the activity of a metallic hydrogenation catalyst. These poisons may be temporary and capable of being removed by some suitable treatment of the catalyst for a short period of time by one or both of the pure reactants; or they may be incapable of being removed by such procedure and will become permanent. For example, traces of oxygen or water vapor in a hydrogen-nitrogen mixture will serve as temporary poisons for an iron catalyst. However, treatment of the catalyst at normal operating temperature by a stream of pure hydrogen or pure hydrogen and nitrogen will rapidly remove this oxygen poison and thus regenerate the catalyst. In contrast to this, during the cracking of hydrocarbons over silica-alumina catalysts, carbonaceous deposits are built

up on the catalysts. These deposits have to be periodically removed by combustion in order to restore the catalyst to its initial activity.

Exact details of the nature of the catalyst surface cannot at the present time be specified. A recent trend tends to classify catalysts as being metals, semiconductors or insulators. This classification throws emphasis on the electronic structure of the solid as a very important one in determining the nature and extent of catalytic action. It is also currently popular to interpret the "active points" or "active regions" of catalysts in terms of lattice defects that have been built up in a catalyst by the addition of impurities, by the removal of certain atoms from the original compounds to produce non-stoichiometric compounds frequently characterized by high conductivity, or by the preparation of the catalyst in such a way as to produce numerous lattice irregularities or dislocations. Much more experimental work will be required before the exact nature of the catalyst surface can be described with any certainty.

To illustrate the types of catalysts and types of reactions that are especially important, a limited number of examples is itemized in the accompanying table. Attention is also called to current commercial use that is being made of certain of the catalysts and reactions.

Mechanism of Catalytic Reactions. From what has so far been stated, it is evident that the mechanism of catalytic reactions must be as obscure as the nature of the catalyst surface itself. Progress is being made in elucidating both the mechanism of the reactions and the nature of the catalyst surface. It seems to be generally agreed that solid catalysts invariably combine chemically at the surface with one or more of the reactants. This combination is referred to as *chemical adsorption* or *chemisorption*. For example, both nitrogen and hydrogen are capable of being chemically adsorbed on iron catalyst at the temperature at which these gases are capable of combining to form ammonia. Silica-alumina cracking catalysts for cracking hydrocarbons in the temperature range of 400° to 500°C are sometimes cited as an exception to this rule. The most recent data, however, seem to indicate that chemical interaction between the reactants and this catalyst surface does actually occur, but takes place on only a very small fraction of the surface of the catalyst.

This has been found true for both the amorphous silica-alumina catalysts and for the silica-alumina molecular sieves that have recently been found to be much more active than the amorphous catalysts and that are being adopted as standard components in commercial cracking catalysts.

The action of the metallic catalyst has for many years been related to the geometric spacing and arrangement of the metal atoms with respect to the molecules of the reactants. Thus, for example, Beeck found that a plot of the spacing of the atoms of pure metal films against the activity of these films for the hydrogenation of ethylene yielded a curve with a maximum corresponding to activities larger by several orders of magnitude than the activity of some metals lower on the curve. Thus, a thin film of rhodium was, per unit area at a given temperature, about 1000 times as active as a thin film of nickel.

Second ed., 1966, edited by G. L. Clark and G. G. Hawley.
 1. Chemistry—Dictionaries. I. Hampel, Clifford A., ed. II. Haw-
 ley, Gessner Goodrich, 1905- ed. 540.3 73-244
 QD5.E58 1973
 ISBN 0-442-23095-8

The Encyclopedia of chemistry.

Library of Congress Cataloging in Publication Data
 Main entry under title:

Van Nostrand Reinhold Company Regional Offices:
 New York Cincinnati Chicago Milbrae Dallas
 Van Nostrand Reinhold Company International Offices:
 London Toronto Melbourne
 Copyright © 1973 by Litton Educational Publishing, Inc.
 Library of Congress Catalog Card Number: 73-244
 ISBN: 0-442-23095-8
 All rights reserved. Certain portions of this work copyright © 1966
 by Litton Educational Publishing, Inc. No part of this work covered
 by the copyright hereon may be reproduced or used in any form
 or by any means—graphic, electronic, or mechanical, including
 photocopying, recording, taping, or information storage and retrieval
 systems—without written permission of the publisher.
 Manufactured in the United States of America
 Published by Van Nostrand Reinhold Company
 450 West 33rd Street, New York, N.Y. 10001
 Published simultaneously in Canada by Van Nostrand Reinhold Ltd.
 15 14 13 12 11 10 9 8 7 6 5 4 3 2

ABELL, Conn.
 ABRAHAM, land,
 ADAMS, Pa. B.
 ADLER, haven
 linking
 AKIN, R.
 de Ne
 Resins
 ALBRIGH
 plating
 ALLEN, Co. T
 Vapor
 ALLEN, J
 biologi
 Electro
 ALLYN, i
 delphia
 ALPER, C
 phia, P
 ALSTON,
 AMIS, Ed
 of Ark
 Transfe
 AMPHLET
 lishmen
 Inorgan
 ANDERSON
 gions L
 APPELMAT
 Argonne
 ASIMOV, I
 Nucleic
 BAB, KE
 tortes, I
 BARCOCCK,
 Boston,
 BACK, R.
 Canada,
 BACKMAN,
 Universi
 the Chei
 BACON, F.
 Carbide
 BALLAR, Jo
 versity o
 questerin
 BARKSDALE,
 BARNARD, /
 Phillipsbl
 Chemical

chemic symp-
ment. Reli-
nified as a
(1), the color
with a protein
ure to light,
e is regener-
vironmen-
have tradi-
hydrocarbons)
is β -caro-
troleinoids in
(ene). Other
des, ketones,
carotenoids
All new struc-
40 structure
ad been pre-
chains, these
est only, due
ss spectrom-
dly changed.
e had been
id not to be
nputities that
organism ex-
tracts on the
v carotenoids
tic rings have
been shown
ich sugars as
obiose.
e carotenoid
carotenoids
varying polar-
ugh some of
il out on crys-
important as
melting point
range, may
enoid might
LC or column

chromatography, its absorption spectrum and its partition coefficient. Structural determinations of new pigments require the use of such instruments as NMR, ORD, IR and the mass spectrometer. A large number of the carotenoids have been synthesized, and thus direct comparisons with authentic samples can be made.

The most characteristic feature is the light absorption spectrum. This may vary from a sharp, 3-peaked spectrum to a single broad peak with examples in between the two extremes. The positions of the maxima in a given solvent, the shape of the curve and the extinction coefficient are a consequence of the basic structure and the type and position of functional groups. Each additional double bond in conjugation results in a displacement of the absorption 15-30 nm toward longer wavelengths. Introduction of a *cis* double bond to the all *trans* system or of a double bond out of plane, as in ring formation, generally results in a shift to shorter wavelengths with loss of extinction. Any functional group that can extend the chromophore, such as a carbonyl in conjugation, will shift the spectrum to longer wavelengths. The chromophore in a polyene chain arises from the possibility of charge separation. If there is a ketonic oxygen that can assume a negative charge, the presence of a proton acceptor, or electron donor such as a protein would stabilize the form. Such a situation exists in the lobster, and the color of the complex is shifted to longer wavelengths and is then blue. On boiling, the complex is broken and the lobster assumes a red color due to the liberation of the red keto-carotenoid astaxanthin.

Cis-trans isomerization. Most of the natural carotenoids are in the all *trans* form, although the natural isomers of phytoene and phytofluene probably contain a central mono-*cis* configuration. Although the most stable isomer is the all *trans* form, stereomutations can occur *in vivo* and *in vitro*. Carotenoids show *cis-trans* isomerism in solution, particularly at elevated temperatures. Light with or without a catalyst (iodine) is quite effective in causing *cis-trans* isomers. It has been calculated that lycopenes with 11 conjugated double bonds could in theory exist in 1,056 different forms. Fortunately only 72 sterically unhindered isomers exist (overlapping of hydrogen atoms vs the overlapping of hydrogen-methyl groups). Some sterically hindered forms have been prepared and have been shown to occur in the metabolism of Vitamin A.

Polycyclopene, proneurosporene and more recently a pro-*f*-carotene have been isolated and shown to be poly *cis*-carotenes.

Function. It is tempting to seek a single universal function for the carotenoids since they are found in such diverse biological forms. Failing this, one is tempted to ascribe some function for these pigments wherever they are found. Thus they have been implicated as an accessory pigment in photosynthesis, as being involved in phototropism in higher plants and in phototaxis in motile cells. They have been suggested as having a function in the reproduction of some fungi and in the protection of other cells, such as bacteria, from absorbed light.

The protective function of the carotenoids in photosynthetic tissues has been well-documented.

In a few cases the carotenoids have been shown to be able to pass on light energy to chlorophyll. Thus, in the diatom *Nitzschia*, light absorbed by the carotenoid fucoxanthin caused fluorescence in chlorophyll a.

While the function of the carotenoids has been proven in a few cases, their function, if any, remains to be determined in a large number of other organisms.

KENNETH L. SIMPSON

References

Goodwin, T. W., Editor, "Chemistry and Biochemistry of Plant Pigments," Academic Press, Inc., London, 1965; cf. chapters by B. C. L. Weedon, T. W. Goodwin, B. H. Davies, C. P. Whittingham, J. H. Burnett, and C. O. Chichester and T. O. M. Nakayama.

"Carotenoids Other Than Vitamin A," 2nd International Symposium, Las Cruces, N.M., IUPAC, Butterworth & Co., Ltd., London, 1969.

MacKinnney, G., "Carotenoids and Vitamin A," in *Metabolic Pathways*, Vol. 2, Ed. D. M. Greenberg, Academic Press, N.Y., 1968.

Porter, J. W., and Anderson, D. G., "Biosynthesis of Carotenoids," in *Annual Review of Plant Physiology*, 18, 197-228 (1967).

Simpson, K. L., Phaff, H. J., Chichester, C. O., Vol. 2, pp. 493-515, Eds. A. H. Rose and J. S. Harrison, Academic Press, London, 1971.

"Carotenoid Pigments in Yeast," in *The Yeasts*, Vol. 2, pp. 493-515, Eds. A. H. Rose and J. S. Harrison, Academic Press, London, 1971.

lys in accelerating chemical processes.

The discussion will be limited to the action of catalysis in accelerating chemical processes.

Strictly speaking, catalysts can either increase or decrease the rate of a reaction. A very large fraction of the literature on catalysis is devoted to systems in which the catalyst increases the rate. The retardation of reactions, called negative catalysis, is known to exist, however. One common theory of the action of negative catalysts is that they combine with and remove from the system traces of positive catalysts, or that they combine with intermediates in a chain reaction in such a way as to break the reaction chain. In the remainder of this description the discussion will be limited to the action of catalysis in accelerating chemical processes.

alter reaction rates.

"loosen up" the bonds of reactants and profoundly chemists, however, that catalysts do in some way There certainly would be no disagreement among nism by which catalysts operate is still not certain. of ordinary chemical reactions. The exact mechanism, however, that the forces involved are probably those "catalytic force." It is now generally recognized, it was decided that catalysis was due to some special to greatly alter the rate of reaction. At the time, bonds of the reactant substances in such a way as name is to the effect that a catalyst loosens the and "lo" meaning loose. The implication of the from two Greek words: "kata," meaning entirely appears to have been well chosen. It was derived and named the phenomenon "catalysis." The name name. Berzelius called these substances "catalysts" 1835, however, that this phenomenon was given a substances by their very presence are able to alter the rate of chemical reactions. It was not until For many years it has been recognized that certain

Thus, the claimed language is definite, because the art has recognized that a composition can be considered a catalyst simply by its ability to alter the rate of a reaction even though the composition changes from the beginning to the end of the reaction. Withdrawal of the rejection is respectfully requested.

CONCLUSION

In view of the above amendments and comments, Applicant respectfully submits that the claims are in condition for allowance. A notice to such effect is earnestly solicited.

Should the Examiner have any questions regarding this matter, he is respectfully requested to contact the undersigned, who is located in the Washington D.C. area at (703) 205-8000.

Pursuant to 37 C.F.R. §§ 1.17 or 1.136(a), Applicant respectfully petitions for a two (2) month extension of time for filing a response in connection with the present application and the required fee of \$380.00 is attached hereto.

If necessary, the Commissioner is hereby authorized in this concurrent and future replies, to charge payment or credit any overpayment to Deposit Account No. 02-2448 for any additional fees

SERIAL NO.: 08/913,218

required under 37 C.F.R. § 1.16 or under 37 C.F.R. § 1.17;
particularly, extension of time fees.

Respectfully submitted,

BIRCH, STEWART, KOLASCH & BIRCH, LLP

By:  #32868

Gerald M. Murphy, Jr.

Reg. No.: 28,977

P.O. Box 747

Falls Church, VA 22040-0747

(703) 205-8000

CD
GMM:GMD:jam

Attachment: Exhibit A

Exhibit A

THE ENCYCLOPEDIA OF
Chemistry

THIRD EDITION

Edited by

CLIFFORD A. HAMPEL

Consulting Chemical Engineer
Skokie, Illinois

GESSNER G. HAWLEY

Formerly Executive Editor
Reinhold Publishing Corporation
Editor Condensed Chemical Dictionary
Eighth Edition



VAN NOSTRAND REINHOLD COMPANY

New York Cincinnati Toronto London Melbourne

Type of Catalyst	Typical Catalysts	Reactions Catalyzed
Acid	Amorphous silica-alumina and crystalline silica-alumina (porous zeolites)	Cracking of hydrocarbons
	HF	Alkylation
	H ₂ SO ₄ , H ₃ PO ₄	Isomerization of hydrocarbons
	H ₃ PO ₄	Polymerization of olefins
Hydrogenation-dehydrogenation	Ni	Oils to fats
	Fe	Ammonia synthesis
	Fe, Co	Hydrocarbon synthesis
	Pt, Pd, Rh	Hydrogenation of double bonds and other carbon linkages
	Fe ₂ O ₃ , MoO ₃ , Cr ₂ O ₃	High-temp. dehydrogenation
	ZnO, Cr ₂ O ₃	Methanol synthesis
Cyclization and aromatization	Pt, MoO ₃ , Cr ₂ O ₃	Heptane to toluene
		Straight-chain hydrocarbons to cyclic and aromatic hydrocarbons
Oxidation	V ₂ O ₅ , MoO ₃ , WO ₃	Partial oxidation of organic compounds
	Bi ₂ O ₃ -MoO ₃	Partial oxidation of propylene to acrolein
	Ag ₂ O	Ethylene to ethylene oxide
	Fe ₂ O ₃ , Cu ₂ O-CuO, Pt, MnO ₂ , Bi ₂ O ₃	Complete oxidation
Hydration-dehydration	Al ₂ O ₃ , ThO ₂	Alcohols to olefins and water vapor, and the reverse
Halogenations	Metallic halides	Deacon process
Dual Type	Pt, MoO ₃ , or Cr ₂ O ₃ on acid type supports	Hydroreforming of hydrocarbons
Polymerization	MoO ₃ on Al ₂ O ₃	Polymerization of olefins to solids
	CrO ₃ on SiO ₂ -Al ₂ O ₃	
	Aluminum alkyls plus titanium halides	

More recently, this difference in activity has been attributed to the electronic characteristics of the individual metals. Beeck showed that his data can be represented as a smooth curve if the logarithm of the activity per unit area of catalyst is plotted against the per cent d-character of the metal, as interpreted by the Pauling hybridized bond theory of metals. In a very spectacular demonstration of the way in which the electronic characteristics of a metal may influence activity, Dowden and Reynolds showed that adding copper to nickel gradually filled the "d-band vacancies" in the nickel and at the same time lowered the activity of the catalyst for the hydrogenation of styrene. As a matter of fact, the activity dropped to approximately zero when enough copper had been added to make the alloy consist of 40 atom % copper and 60 atom % nickel. This result was interpreted as indicating that one or both of the reactants on the catalyst surface tended to transfer electrons into the lattice of the solid. It must be pointed out, however, that for the hydrogenation of other molecules, catalysts containing certain amounts of copper are definitely more active per unit area than nickel itself. For example, the rate of hydrogenation of ethylene to ethane has been reported to be manifold greater for catalysts containing 20 to 80 atom % copper than for pure nickel.

For oxide catalysts, such as vanadium pentoxide, molybdenum trioxide, zinc oxide, and chromium oxide, evidence is accumulating to indicate that the steady state composition of the solid which cata-

lyzes a reaction is definitely different from that of the original stoichiometric compound. It is also known that the electrical conductivity of these compounds changes by many orders of magnitude as lattice defects are built up. These defects, in some instances, are produced by adding excess oxygen (p-type semiconductors) and in some instances by removing atoms from the initial stoichiometric compound (n-type semiconductors). Although definitive data for correlating the conductivity of a semiconductor with its activity as a catalyst are for the most part still lacking, there seems to be little doubt that the creation of lattice defects is important in and perhaps essential to the catalytic action of solids. Some workers in the field believe that all catalytic reactions are controlled essentially by the electronic characteristics of the solids. Others admit that certain reactions are so controlled, but that some reactions may take place by mechanisms that are not concerned with the conductivity of the solids.

In conclusion, it may be well to mention a few of the newer research tools that are now available to help unravel the factors that are important in producing active catalysts. These include methods for measuring the surface area of a finely divided or porous catalyst (see BET Theory); for measuring the pore size and pore distribution of catalyst; and for obtaining values of the electrical properties of the catalyst particles.

In addition x-ray and electron diffraction, electron microscopy, field emission and ion emission

mic
prob
mag
let a
give
and
chem
Fi
trace
tain
trace
aldehy
tablis
meta
of an
tion
ious
medi
of th
tion
Hor
gene
that
catal
to in
comp
gases
ampl
decor
takes
posin
The
with
nitro
until
decor
gover
pente
In
solut
much
lysis
with
jected
terize
nome
tion,
actan
fects
the p
some
Mc
for c
These
dation
plex
reacti
by pr
by hy
ample
In
decor
ing ca
those
conne
cally
to ha
centra